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Effect of Limestone Type and Grind on SO2 Scrubber Performance

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16. ABSTRACT

The paper describes the effect of limestone type and grind on SO2 scrubber performance. It gives results of a comparison of the amount of limestone feed required as a function of particle size, to obtain a given SO2 removal efficiency and, thus, to verify the relative magnitude of the effect of limestone grind observed during an earlier study. Experimental data were also obtained with limestones from four different quarries ground to similar sizes to test the geological or type effect on limestone reactivities. It also gives results of a test of the effectiveness of wet screen analysis as a means of classifying limestone grinds for scrubber use. A mass-transfer model and Coulter-counter particle-size distribution data were also tested as a means of defining limestone reactivities. The cost-reduction effect of finer limestone grinding on SO2 scrubber efficiency was found to be considerable.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Sulfur Oxides	Stationary Sources	07B
Scrubbers	Wet Screens	07A, 13I
Limestone	Coulter Counters	08G
Analyzing		14B
Mass Transfer		14G
Particle Size Distribution		

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Effect of Limestone Type and Grind on SO_2 Scrubber Performance

The cost-reduction effect of finer limestone grinding on SO_2 scrubber efficiency can be very considerable.

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INTRODUCTION

Because of its low price and high availability, limestone slurry is the most commonly used reagent for wet flue-gas desulfurization (FGD) processes. In addition to the newly developed Dowa (*1*) and Chiyoda Thoroughbred-121 (*2*) processes, limestone slurry is used in conventional lime/limestone and dual alkali-scrubber processes to neutralize the absorbed sulfur dioxide. However, limestone is not a very reactive reagent, because it does not completely dissolve in the scrubber system. Usually, more than 20 percent of the added limestone is disposed of with the $CaSO_3/SO_4$ sludge (*3*). Poor limestone utilization not only increases FGD operating cost and solid-waste disposal volumes but also decreases system reliability. Several factors can affect the limestone dissolution rate, or reactivity, such as limestone type and grind, temperature, pH, partial pressure of dissolved CO_2, buffer additives, and impurities [*4-9*]. Since the limestone dissolution rate is influenced by these factors, SO_2 scrubber performance may be similarly affected. Since conventional limestone scrubbing is the most popular process among commercialized FGD systems [*10*] and scrubber performance is relatively sensitive to the limestone utilization rate [*11*], the present paper focuses attention on the effects of limestone type and grind on the performance of the conventional limestone scrubber.

Limestone used in a scrubber system is crushed into small particles to increase the solid/liquid contact area and, thus, the dissolution rate. When a certain limestone is to be ground for use in an SO_2 scrubber, the major concerns are:

1) How significantly can the limestone grind affect scrubber performance? Does an improvement in limestone utilization or SO_2 removal efficiency warrant the economic penalty of finer grinding?

2) How can the limestone grind be classified? Is a wet screen analysis capable of characterizing the limestone particle-size distribution?

3) Is there a geological effect on limestone reactivity? Is there a difference in the dissolution rate or reactivity of limestones from different quarries when ground to the same grade?

A preliminary TVA study [*12*] emphasized the importance of these concerns. Assuming that stoichiometric ratios of 1.15, 1.35, and 1.55 represent the limestone feed requirement to attain a given SO_2 removal with grinds of 95 percent −325 mesh, 90 percent −200 mesh, and 70 percent −200 mesh, respectively, the TVA study concluded that economics favored fine grinding. Thus, the higher capital investment needed for the grinding equipment to produce the smaller limestone particles is more than offset by the lower costs of waste disposal and raw limestone makeup.

The major objective of this paper is to compare the amount of limestone feed required as a function of particle size, to obtain a given SO_2-removal efficiency and, thus, to verify the relative magnitude of the effect of limestone grind observed during the TVA study. Experimental data were also obtained with limestones from four different quarries ground to similar sizes, 90 percent −325 mesh and 70 percent −200 mesh, to test the "geological" or "type" effect on limestone reactivities.

The second objective of this paper is to test the effectiveness of wet screen analysis as a means of classifying limestone grinds for scrubber use. A mass-transfer model and Coulter-counter particle-size distribution data were also tested as a means of defining limestone reactivities.

EXPERIMENTAL

All experiments were performed on the EPA/IERL-RTP pilot-scale limestone scrubber system. The scrubber is a turbulent contact absorber (TCA) with 7.5 m^3/min flue-gas capacity (0.1 MW). No fly ash was present in the flue gas, which was drawn from a gas-fired boiler and injected with pure SO_2 and HCl. The oxygen content of the flue gas was controlled in the range of 6 to 7 percent. The scrubber system was set up in the single-loop configuration shown in Figure 1. The major scrubber test conditions are listed in Table 1. The TCA contained three beds of nitrile-foam spheres and operated at a slurry recirculation rate of 63.5 liter/min. A bleed stream of the slurry from the hold tank was directed to the clarifier and then processed by a rotary-drum vacuum filter to remove the precipitated waste and return all filtrate to the scrubber in a fully closed-loop operating mode.

Each run consisted of approximately 100 hours of continuous, steady-state operation. The principal response measured for these tests was SO_2 removal. Both wet sampling (modified EPA standard Method 6) and ultraviolet analysis (DuPont 400 SO_2 analyzer) were used to deter-

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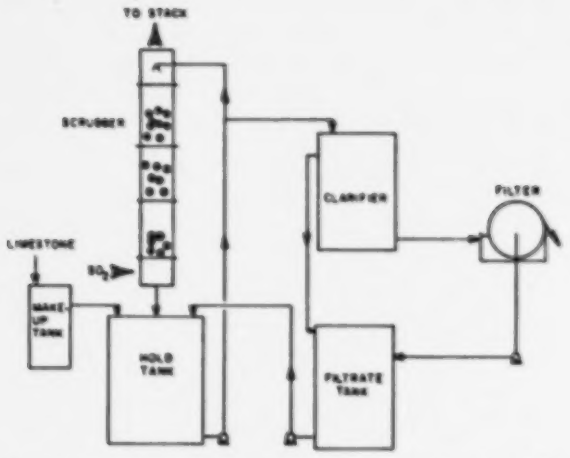

Figure 1. Flow diagram for single-loop scrubber configuration of the limestone—TCA system at EPA/IERL-RTP.

TABLE 1. MAJOR OPERATING CONDITIONS OF LIMESTONE-TYPE AND GRIND TEST

Scrubber	= TCA with three beds of nitrile foam spheres
Scrubber ΔP	= 20 cm-H_2O
L/G ratio	= 6.68 liter/m^3
Inlet SO_2	= 2800 ppm
Cl concn. in liquor	= 3000 ppm*
Slurry solids	= 9 percent
Hold tank residence time	= 9 minutes

* Controlled by pure HCl injection into flue gas.

mine the SO_2 concentration in the flue gas entering and leaving the scrubber. Limestone makeup slurry was fed at several different rates in order to vary the stoichiometric ratio. This ratio was defined as:

$$\text{stoichiometric ratio} = \frac{1}{\text{utilization}}$$

$$= \frac{\text{moles of } CaCO_3 \text{ fed}}{\text{moles of } SO_2 \text{ absorbed}} \quad (1)$$

Slurry solids were collected from both hold tank and filter cake. Chemical analysis of the solids provided sulfur, carbon, and calcium contents so that stoichiometric ratios could be estimated and compared with those from material balances.

Four grinds of Fredonia limestone from Fredonia, Kentucky, were tested. A summary of particle-size distributions, as analyzed by the wet screen method at RTP, is presented in Table 2. Three other types of limestone—Longview from Alabama, Stone Man from Tennessee, and Georgia marble from Alabama—were also tested. These stones were ground to two grades, fine and coarse. Results of chemical and wet screen analyses of all types and grinds of limestone tested are listed in Tables 3, 4, and 5. Table 3 shows that all four types of limestone have similar chemical compositions. Tables 4 and 5 also show that all fine- and coarse-grind limestones have similar particle-size distributions, according to wet screen analysis, within a range of 70 mesh (210μm) to 325 mesh (45μm).

Energy requirement is a major factor determining the cost of and economic benefit from the grinding of limestone to various grades. The TVA economic study evaluated cases with energy requirements ranging from 5 to 15 kWh per metric ton of coarsely ground limestone and assumed that fine grinding would consume three times as much energy for each type of limestone. As shown in Table 6, the actual energy used for the four types of coarse limestone tested at RTP ranged from 6 to 12.8 kWh/metric ton. All of them are within the scope of TVA premises. Also, the actual energy consumption for fine grinding is less than that assumed by TVA. All the above analyses show that the TVA economic study can be applied to the four types of limestone tested and, if the limestone grind effect is verified by RTP data, the economic gain estimated by TVA may be conservative.

RESULTS AND DISCUSSION

Experimental results of the limestone type and grind tests are shown in Figures 2, 3, and 4. The relative limestone reactivities can be obtained directly from the plot of SO_2 removal (scrubber performance) vs. limestone stoichiometric ratio (limestone feed rate). As the reactivity of the limestone increases, less limestone is required for a certain rate of SO_2 removal. Thus, at a fixed stoichiometric ratio, a more reactive limestone should absorb more SO_2.

Limestone Grind Test

Four grinds of Fredonia limestone were used for the test. Figure 2 shows that limestone grind has a distinct effect on SO_2 scrubber performance. The relative ranking of limestone reactivity is: Feedbelt = Fine > Coarse > Very coarse. Comparison with the limestone size data (Table 2) indicates that limestone reactivity can be improved significantly by finer grinding within the range tested. Yet the large gain of SO_2 removal from Fredonia Very Coarse to Coarse is more than expected, because the difference between wet sieve analysis particle-size distribution of the two grinds is too small to be consistent with the observed relative reactivities.

Fredonia Feedbelt (89 percent less than 325 mesh) is the finest of the four grinds tested. The comparison of scrubber performance (Figure 2) shows that the SO_2 removal efficiency of Fredonia Feedbelt is very close to that of Fredonia Fine. Compared with the significant improvement of scrubber performance from Coarse to Fine Fredonia, the difference between Fine and Feedbelt Fredonia is negligible. This may imply that Fine grind (84 percent −325 mesh) represents the limit of limestone grind effect with Fredonia limestone. Further grinding from 84 percent to 89 percent −325 mesh may not be worthwhile.

The Fredonia Fine limestone used in the RTP scrubber tests lies between the finest grind (95 percent −325 mesh) and the medium grind (90 percent −200 mesh) that were considered by TVA in their economic evaluation of the effect of grind size. Since the TVA premises assumed

TABLE 2. SUMMARY OF WET SIEVE PARTICLE SIZE ANALYSES OF FREDONIA LIMESTONE

Nominal Grind	Weight Percent −325 mesh	−230 mesh	−200 mesh	−100 mesh	−70 mesh
Feedbelt	88.6	96.0	97.4	99.5	99.9
Fine	84.1	94.1	95.3	97.7	98.1
Coarse	54.5	66.2	69.6	92.9	97.1
Very coarse	51.2	62.0	65.0	88.4	95.4

TABLE 3. LIMESTONES USED IN TYPE AND GRIND TESTS

Limestone Source	Location	Chemical Composition, wt. percent			
		Calcium (Ca)	Magnesium (Mg)	Carbonate (CO_3)	Acid Insolubles
Fredonia Quarries	Fredonia, Kentucky	35.8	2.5	60.5	2.2
Georgia Marble	Sylacauga, Alabama	38.8	0.5	59.2	2.0
Longview Lime Company	Longview, Alabama	38.2	0.7	59.9	1.0
The Stone Man	Chattanooga, Tennessee	36.4	1.0	57.2	4.1

TABLE 4. SUMMARY OF WET SIEVE PARTICLE SIZE ANALYSES OF FINE GROUND LIMESTONE

Limestone Type	Percent Weight		
	−325 mesh	−200 mesh	−100 mesh
Fredonia	84.1	95.3	97.7
Longview	84.6	98.1	99.9
Stone Man	82.9	98.7	98.8
Georgia Marble	84.1	98.6	99.9

TABLE 5. SUMMARY OF WET SIEVE PARTICLE SIZE ANALYSES OF COARSELY GROUND LIMESTONE

Limestone Type	Percent Weight		
	−325 mesh	−200 mesh	−100 mesh
Fredonia Coarse	54.1	69.6	92.9
Fredonia Very coarse	51.2	65.0	88.4
Longview	58.2	70.9	93.4
Stone Man	52.9	71.6	96.4
Georgia Marble	48.1	70.1	94.7

TABLE 6. COMPARISON OF LIMESTONE GRINDING ENERGY REQUIREMENTS

Grind	Coarse	Fine	
Energy Reqirement Type	kWh/ton* (actual)	kWh/ton* (assumed)	kWh/ton* (actual)
Fredonia	7.52	22.56	18.3
Longview	12.0	36.0	32.1
Stone Man	12.8	38.4	20.6
Georgia Marble	6.0	18.0	12.4

*Metric tons.

stoichiometric requirements of 1.15 and 1.35, respectively, for those grinds, it is necessary to interpolate a stoichiometric ratio of 1.25 to represent the limestone feed requirement for the Fredonia Fine grind, which is 84 percent −325 mesh, 95 percent −200 mesh by RTP analysis. The Coarse grind Fredonia used in the RTP scrubber tests (70 percent −200 mesh) is close enough to the coarsest grind evaluated by TVA so that the stoichiometric ratio can be compared directly with the 1.55 value used in their economic study.

Referring to the RTP scrubber results on the effect of grind, as shown in Figure 2, a stoichiometric ratio of 1.25 should yield a SO_2-removal efficiency of 84 percent with Fredonia Fine. The same removal efficiency would require a stoichiometric ratio of about 1.7 with Fredonia Coarse grind—more than that assumed in the TVA evaluation. It is concluded from these comparisons that the TVA economic study made adequate estimations of the stoichiometric requirements of Fine and Coarse grinds of Fredonia limestone and, accordingly, the economic benefit from grinding Fredonia limestone from 70 percent −200 mesh to 95 percent −200 mesh was confirmed experimentally.

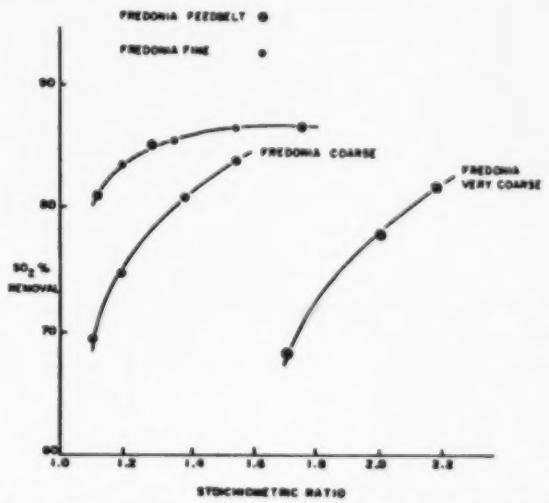

Figure 2. Performance of the TCA scrubber with Fredonia limestone.

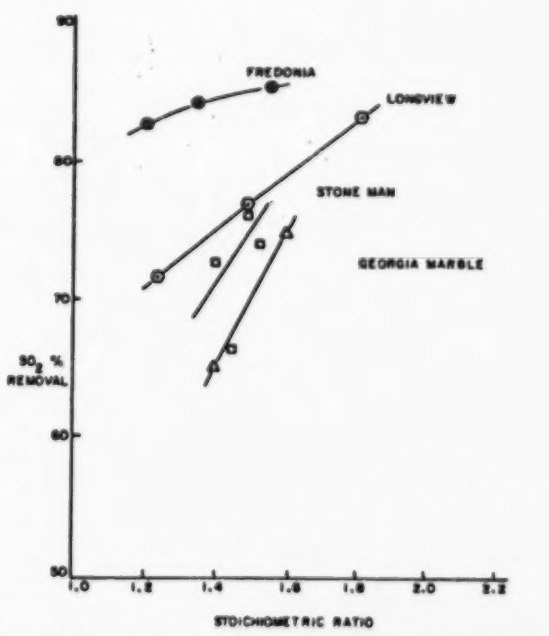

Figure 3. Performance of the TCA scrubber with fine-grind limestone.

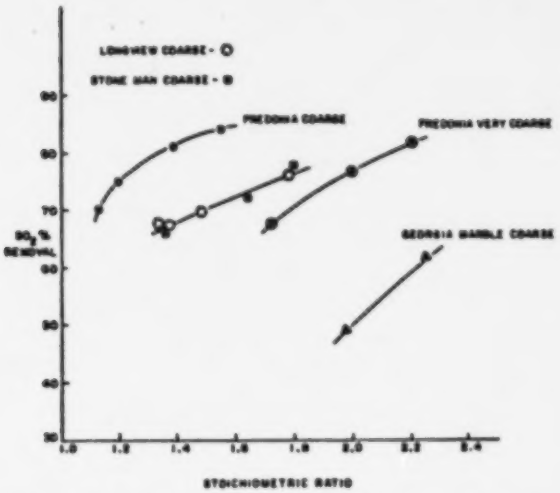

Figure 4. Performance of the TVA scrubber with coarse-grind limestone.

Limestone Type Test

Four types of limestone—Fredonia, Longview, Stone Man, and Georgia Marble—were tested for their reactivities under the operating conditions shown in Table 1. The performances of the RTP scrubber with fine- and coarse-grind limestone are shown in Figures 3 and 4, respectively. All the finely ground limestone was more reactive than the coarsely ground, as observed in the previous grind test. For Longview limestone, stoichiometric ratios of about 1.25 for fine grinds and 1.6 for coarse grinds would be required to obtain 72 percent SO_2 removal. The relative stoichiometric ratios are very close to those assumed by the TVA economic study (1.25 and 1.55, respectively). Therefore, the conclusion that there is an economic benefit from finer grinding can be applied to Longview limestone.

Significant differences were observed among the reactivities of the four types of limestone with the same grind. The order of relative reactivity of finely ground limestone is: Fredonia > Longview > Stone Man > Georgia Marble. The relative ranking of scrubber performances when using the coarsely ground stones was similar to that with fine grind, except that the difference between Longview and Stone Man was almost negligible.

The results of wet screen analyses of the four finely ground limestones tested at RTP are shown in Table 4. Most of them are 84 percent less than 325 mesh. No significant difference in particle-size distribution can be seen from the wet sieve analysis results, but notable differences in scrubber performance were observed when those four types of limestone were applied to the RTP SO_2 scrubber. At this point, however, it is still uncertain whether the different scrubber performances can be attributed to the "limestone-type" or "geological" effect. Because sieve analysis covers only the fraction of limestone with particle size larger than 325 mesh (45μm), about 84 percent of the finely ground and 50 percent of the coarsely ground limestone was not sized by sieve analysis. Those fine fractions of limestone may play an important role in the dissolution rate since mass-transfer theory indicates that small particles dissolve faster than large ones.

It is obvious from the previous analysis that, in order to define the limestone grinds more precisely, the particle-size distribution must be measured by some method more rigorous than sieve analysis. Coulter-counter particle-size analysis is a method which can measure particle size down to the submicron range. It was found that the particle-size distribution by Coulter-counter analysis could characterize most of the fine fraction of limestone not included in the wet sieve analysis. To provide complete particle-size distribution, the Coulter-counter data were combined with wet sieve analysis data for all four types of stones, as shown in Table 7, and a limestone dissolution model was

Table 7. Differential Particle Size Distributions, Volume Percent

Mean Particle Size(μm)	Fredonia				Georgia Marble		Longview		Stoneman	
	Feedbelt	Fine	Coarse	Very Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
0.707	0.400	0.000	0.400	0.180	0.000	0.000	0.100	0.600	0.260	0.100
0.891	0.700	0.240	0.500	0.270	0.000	0.200	0.100	0.600	0.440	0.400
1.12	1.300	0.850	1.100	0.630	0.100	0.300	1.200	1.100	1.070	0.900
1.41	2.400	2.190	1.900	0.990	0.200	0.400	2.000	1.900	1.800	1.400
1.78	3.900	4.440	3.100	1.800	0.300	0.700	2.700	2.500	2.390	1.800
2.25	5.900	5.530	4.200	2.620	0.500	0.900	3.000	3.000	2.610	2.000
2.83	7.900	9.060	5.100	4.050	0.800	1.200	3.800	3.600	2.800	2.000
3.56	8.500	10.510	5.000	4.960	1.200	1.600	4.700	4.700	3.240	2.100
4.49	7 500	8.020	3.600	4.593	2.000	1.800	4.900	5.300	3.060	2.000
5.66	6.600	5.110	2.800	3.510	2.400	1.600	5.500	5.700	3.020	1.900
7.13	5.900	4.130	2.300	2.970	3.400	1.800	5.500	5.300	3.500	2.000
8.98	5.700	3.890	2.000	2.620	4.400	2.500	5.800	5.000	3.900	2.400
11.3	5.200	3.610	2.000	2.710	6.000	3.200	6.300	3.800	4.830	3.000
14.3	4.800	3.710	2.200	3.060	8.600	4.300	6.400	4.400	6.240	4.00
18.0	4.700	3.910	2.900	3.240	11.100	5.100	6.700	4.000	7.730	4.900
22.6	4.700	3.910	3.200	3.600	12.600	5.900	6.800	3.700	8.920	5.600
28.5	4.600	4.530	4.000	3.960	14.300	7.700	6.900	3.900	11.380	5.500
35.9	4.500	4.580	4.600	4.140	13.200	8.500	7.600	3.800	11.600	7.100
45.3	4.500	5.450	5.600	5.580	10.200	9.600	8.300	4.200	11.450	8.300
57.0	3.800	5.190	7.000	6.300	4.800	9.800	6.300	4.900	6.840	7.500
71.8	3.500	4.630	7.100	6.300	2.600	9.000	4.000	4.400	2.450	9.000
90.5	1.700	3.760	8.700	7.380	1.300	8.400	1.100	6.300	0.450	10.000
114.	1.200	2.340	8.300	8.290		6.700	0.300	8.700		8.500
144.	0.100	0.300	4.900	6.300		4.800		6.700		4.100
181.		0.100	3.400	4.960		3.000		1.600		1.500
228.			1.900	2.970		0.600				0.700
287.			0.900	1.240		0.100				0.200
362.			0.600	0.500		0.100				0.100
456.			0.300	0.300						
575.			0.100							

utilized to predict the relative limestone reactivities from the size-distribution data.

Mass-Transfer Model

Toprac and Rochelle [13] developed and tested a mass-transfer model which can be used to estimate relative reactivity of different limestones as a function of particle-size distribution. For a given size fraction, j, with initial average diameter, d_j, and initial average volume, V_j, the dissolution rate is given in terms of the fraction of undissolved $CaCO_3$, f_j:

$$\frac{df_j}{dt} = -\frac{kf_j^{2/3}}{V_j^{1/3}} - \frac{kBf_j^{2/3}}{V_j^{1/3}} \qquad (2)$$

The first term of this equation represents dissolution in an infinite stagnant solution and dominates for small particles. The second term represents dissolution in an agitated system and dominates for large particles. The constant k is a function of solution composition. The constant B depends primarily on agitation. A nominal level of agitation in the absence of CO_2 participation in mass transfer gives B equal to 400 cm^{-1} [13].

Equation (2) can be integrated to give the time required to get a given f_j:

$$t = \frac{3}{kB^2}\left[\ln\left(\frac{1 + BV_j^{1/3}f_j^{1/3}}{1 + BV_j^{1/3}}\right) + BV_j^{1/3}(1 - f_j)\right] \qquad (3)$$

Because the scrubber system has a large circulation rate relative to the feed rate of limestone slurry, it can be treated as a continuously stirred tank reactor (CSTR). The probability that a limestone particle will be in the system for time t is given by:

$$P(t)dt = \frac{1}{\tau}e^{-t/\tau}dt \qquad (4)$$

The average residence time τ is the total Ca inventory in the system divided by the limestone feed rate.

The total fraction of undissolved $CaCO_3$ (F) can be obtained by integrating over all possible times for each size fraction and by summing over all size fractions:

$$F = \sum_{j=1}^{m} \phi_j \frac{1}{\tau}\int_0^\infty e^{-t/\tau} f_j dt \qquad (5)$$

The weight fraction of each size fraction is given by ϕ_j. The variable f_j is an implicit function of t given by Equaton (3).

Equation (5) can be simplified by transforming from an integration over t to an integration over f_j:

$$F = \sum_{j=1}^{m} \phi_j \frac{1}{\tau}\int_1^0 \frac{f_j e^{-t/\tau}}{df_j/dt}\,df_j \qquad (6)$$

In this numerical integration, t is a function of f_j given by Equation (3) and df_j/dt is a function of f_j given by Equation (2). The integral over f_j was evaluated in this work by direct numerical integration with an f_j step size of 0.01. This step size gave good values of F for F less than 0.7.

For a given limestone, F can be determined as a general function of k_1. The stoichiometric ratio, SR, is given by $1/(1 - F)$. If two different limestones gave the same SO_2 removal, the solution composition was assumed to be the same, so were the values of k. However, for constant hold-tank volume and a constant concentration of calcium solids (moles Ca/liter solution), the residence time, τ, will be inversely proportional to the stoichiometric ratio. Therefore, the quantity $k_1 \cdot SR$ should be constant at a given SO_2 removal. The reciprocal of this quantity, $(k_1 \cdot SR)^{-1}$, is defined as the relative reactivity. SO_2 removal should increase with increasing relative reactivity.

The particle-size distributions used in this model are given in Table 7. A Model TAII Coulter Counter was used to determine size distribution from 0.7 to 160 μm by overlapping distributions obtained with 30, 100, and 400 μm apertures. The samples were run in 0.18 M $CaCl_2$ electrolyte to minimize dissolution during sizing. Wet screening was used to obtain size fractions above 160 μm.

Figures 5, 6, and 7 give calculated stoichiometric ratios as a function of relative reactivity for all the limestone types and grinds tested in the RTP pilot plant. Direct comparisons can be made between these data and the experimental results shown in Figures 2, 3, and 4 because more reactive limestone should be able to bring about higher SO_2 removal efficiency at a fixed stoichiometric ratio.

The relative reactivities for the four grinds of Fredonia limestone are shown in Figure 5. The reactivity of fine fredonia is higher than that of coarse and very coarse Fredonia. This is in accordance with the scrubber performance observed at RTP (Figure 2), but the improvement of scrubber performance from Fine to Feedbelt is insignificant. One possible explanation is that the scrubbing liquor is getting closer to the equilibrium point with finer limestone grinding. The equilibrium point represents the upper limit of the dissolved alkalinity or SO_2 removal efficiency that can be derived from limestone dissolution.

Significant differences in relative reactivities of four types of fine-grind limestones are predicted by a mass-

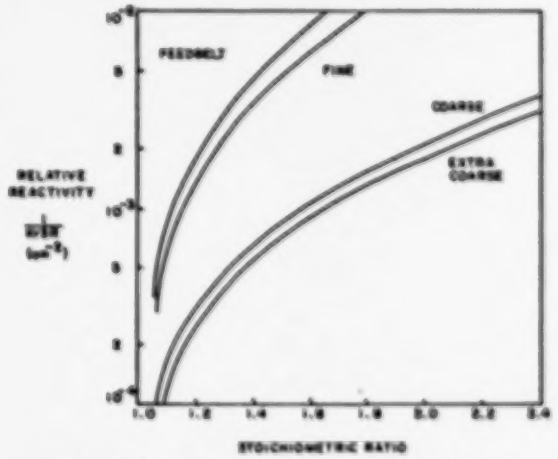

Figure 5. Relative reactivities of four grinds of Fredonia limestone.

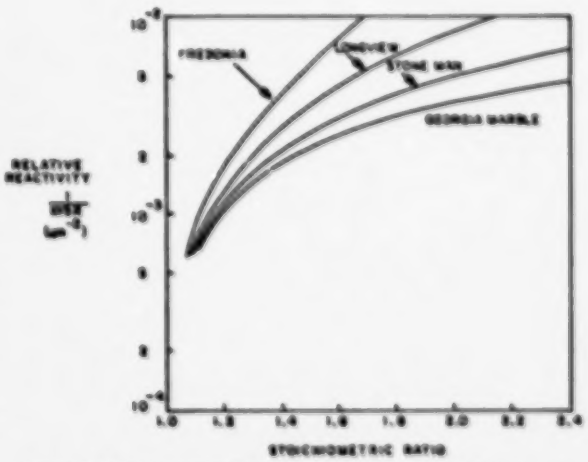

Figure 6. Relative reactivities of four types of fine grind limestones.

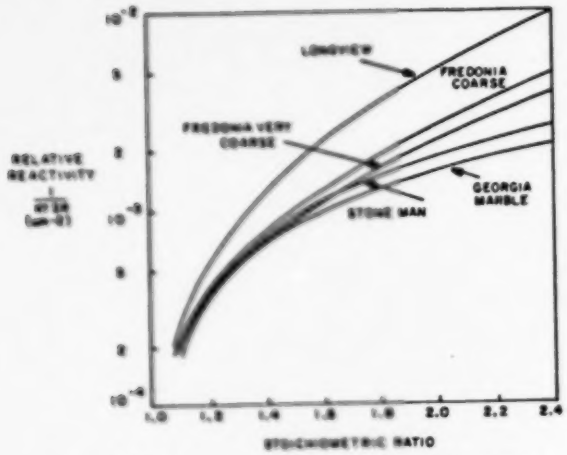

Figure 7. Relative reactivities of coarsely ground limestones.

transfer model as shown in Figure 6. Furthermore, the relative ranking of the four limestones is in accordance with the pilot plant data shown in Figure 3. This indicates that mass-transfer model can predict the relative reactivities of different types of limestone for which sieve analysis cannot measure the difference. This also shows that differential scrubber performance for various types of finely ground limestone observed at RTP is not necessarily due to the "geological effect," but is more likely the result of differences in size distribution of particles smaller than 30 μm. The mass-transfer model also predicts noticeable differences in the reactivities of coarsely ground limestones (Figure 7) but they cannot fit the experimental data (Figure 4). The discrepancy can be attributed to either erroneous particle-size distribution measurement or inconsistent scrubber operation.

CONCLUSIONS

The following conclusions can be drawn from this work:

1) The limestone grind effect on SO_2 scrubber performance was verified by experimental data. Finer grinding of limestone can increase limestone reactivity and, thus, reduce the quantity of both the limestone required and the waste sludge produced for a given SO_2 removal. The economic benefit of using fine (85 percent −325 mesh) instead of coarse (70 percent −200 mesh) limestone, as derived from the TVA economic study, was supported by RTP data.

2) An upper limit of limestone grind effect was observed with the data from Fredonia Fine testing. Further grinding of Fredonia limestone from 85 percent −325 mesh to 89 percent −325 mesh did not affect the SO_2 scrubber performance.

3) Wet sieve analysis to 45 μm is not sufficient to classify the relative grind of limestones. The Coulter counter was found to be an effective method to measure the particle-size distribution of limestone particles with diameters less than 160 μm.

4) The relative reactivities of finely ground limestones can be predicted by a limestone-dissolution model utilizing both the wet sieve analysis and Coulter counter data.

5) The limestone-type effect can be partially explained by the relative reactivities estimated from the mass-transfer model. A refined limestone-dissolution model and more complete and accurate particle-size distribution data are required to investigate further the limestone-type effect, especially for coarsely ground limestones.

NOTATION

B	=	mass to transfer agitation parameter, cm^{-1}
d	=	particle diameter, μm
f	=	fraction $CaCO_3$ undissolved
F	=	total fraction $CaCO_3$ undissolved
k	=	mass-transfer rate constant, cm^3/sec
P	=	probability of time t
SR	=	stoichiometric ratio
t	=	time, sec
V	=	initial particle volume, cm^3
τ	=	calcium residence time, sec
ϕ	=	volume fraction of limestone

Subscript

j	=	jth size fraction of limestone

LITERATURE CITED

1. Jackson, S. B., C. E. Dene, and D. B. Smith, "Dowa Process Tests, Shawnee Test Facility." Sixth EPA Symposium on Flue Gas Desulfurization, Houston, Texas (October 28-31, 1980).
2. Morasky, T. M., D. P. Burford, and O. W. Hargrove, "Results of the Chiyoda Thoroughbred-121 Prototype Evaluation," Sixth EPA Symposium on Flue Gas Desulfurization, Houston, Texas (October 28-31, 1980).
3. Leivo, C. C., J. E. Williams, and K. R. Durkee, "Flue Gas Desulfurization Systems: Design and Operating Considerations, Vol. II," Technical Report, EPA-600/7-78-030b (NTIS PB280254) (March, 1978).
4. Erga, O. and S. G. Terjesen, *Acta. Chem. Scand.*, **10**, 872-74 (1956).
5. Berner, R. A. and J. W. Morse, *Am. J. of Sci.*, **274**, 108-134 (1974).
6. Kim, Y. K., M. E. Deming, and J. D. Hatfield, *Env. Sci. and Tech.*, **9**, 949 (1975).
7. Barton, P. and T. Vatanatham, *Env. Sci. and Tech.*, **10**, 262 (1976).
8. Plummer, L. N., T. M. L. Wigley, and D. L. Parkhurst, *Am. J. of Sci.*, **278**, 179-216 (1978).
   Sjoberg, E. L., *Geo. Cosmo. Acta*, **40**, 441-47 (1976).
9. Chan, P. K. and G. T. Rochelle, "Limestone Dissolution—Effects of pH, CO_2, and Buffers Modeled by Mass Transfer," ACS National Meeting, Atlanta, Ga. (March 29-30, 1981).
10. Smith, M. P., M. T. Melia, B. A. Laseke, Jr., and N. Kaplan, "Recent Trends in Utility Flue Gas Desulfurization," Sixth EPA Symposium on Flue Gas Desulfurization, Houston, Texas (October 28-31, 1980).
11. Head, H. N., S. C. Wang, and J. E. Williams, "EPA Alkali Scrubbing Test Facility: Advanced Program, Fourth Progress Report, Vol. 1, Basic Report EPA-600/7-79-244a (NTIS PB80-117906) (November, 1979).
12. Little, A. F. (TVA) letter to J. E. Williams (EPA/IERL-RTP) "Preliminary Evaluation of the Effect of Limestone Grind Size Upon the Economics of Limestone Scrubbing FGD Facilities" (December 6, 1977).
13. Toprac, A. J. and G. T. Rochelle, "Limestone Dissolution in Stack Gas Desulfurization Process—Effect of Type and Grind," Presented at the AIChE Annual Meeting, New Orleans, La. (November 8-12, 1981).

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